Utilization of crude karanj (*Pongamia pinnata*) oil as a potential feedstock for the synthesis of fatty acid methyl esters

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ABSTRACT

Methyl esters were synthesized from crude karanj oil (CKO) by single step esterification with methanol using sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) as catalysts in a homogeneous batch process. H_3PO_4 was less active than H_2SO_4 during the process as it presented very low ester yields (<20%) for the various molar ratios of fatty acid to alcohol studied. With H_2SO_4 as catalyst, the yield was as high as 89.8% at 65 °C after 5 h. The fatty acids profile of the oil (palmitic acid: ∼12%; stearic acid: ∼8%; oleic acid: ∼52% and linolenic acid of 17%) and the different reactivities of the acids were responsible for the observed differences in conversion to methyl esters. The findings attained with this study might contribute to the economic utilization of a non-edible feedstock.

1. Introduction

Fatty acid methyl esters (FAME) (biodiesel), obtained from vegetable oils of edible and non-edible sources, have been introduced as a promising substitute to fossil fuels. Their combustion is environmentally more benign than that of petroleum-based fuel, they offer less storage difficulties, have a high cetane number and flash point and possess excellent lubrication characteristics (Hameed et al., 2009; Mustafa, 2007). FAME is typically synthesized via catalytic transesterification and/or esterification of animal fats, vegetable or waste cooking oils with short chain alcohols (mostly methanol). The high value of edible vegetable oils as a food product makes their utilization for the synthesis of cost-effective FAME very challenging (Canakaci and Gerpen, 2001). Furthermore, if edible oil is employed in biodiesel industry, the world food market is affected. Biodiesel is also expensive due to such issues as equipment and processing conditions (Asakuma et al., 2009; Szulczyk and McCarl, 2010). Thus, the utilization of such oils for biodiesel production in some developing countries with limited arable land per capita is not economic or even prohibited (Lin et al., 2011). In order to address the shortages of feedstock for the production of biodiesel, new non-edible oil sources need to be exploited (Lin et al., 2011; Mustafa, 2011). For example, karanj (*Pongamia pinnata*) oil, a high

fatty acid non-edible oil can be employed to produce biodiesel (Sharma and Singh, 2008; Naik et al., 2008; Nabi et al., 2009).

Crude karanj oil (CKO) is extracted from the seeds of the plant, and has found applications in body oils, salves, lotions, soaps, hair tonics, shampoos and pesticides (Kesari et al., 2010). This enduring plant thrives in tropical conditions and is now found in India, Malaysia, Thailand, Vietnam, Australia, Florida, Hawaii, The Seychelles, Oceania and The Philippines (Mukta and Sreevalli, 2010). CKO is considered to be less toxic and cheaper than jatropha oil, so it has become the subject of biodiesel research (Karmee and Chadha, 2005; Naik et al., 2008; Sharma and Singh, 2008).

The industrial value of vegetable oils depends on their fatty acids composition and the ease with which it can be modified (Berchmans and Hirata, 2008; Ramos et al., 2009). CKO contains no less than 23% saturated fatty acids (myristic, stearic and palmitic acid) and more than 73% unsaturated fatty acids (oleic, linoleic and arachid oleic acid). For example, it contains more mono-unsaturated oleic acid (51.59%) than other non-edible oils such as tung oil (8.0%), jojoba oil (11.0%), neem oil (45.55%) and jatropha oil (44.7%). While feedstock with a low level of free fatty acids (FFAs) can be alkali catalyzed during the biodiesel production process, feedstocks with significant FFAs amounts perform better in the presence of acid catalysts (Demirbas, 2009).

Thus, the present study investigated FAME synthesis using non-edible, high fatty acid CKO under mild conditions by employing conventional Brönsted acids, sulfuric and phosphoric acid as homogeneous catalysts in the esterification of CKO with methanol.

2. Methods

2.1. Chemicals and physiochemical properties of karanj oil

Crude karanj oil (CKO) was supplied by TelagaMadu Resources Ltd., Malaysia. Sulfuric acid (95–98%) was purchased from R & M Chemicals, Ltd. Malaysia. Phosphoric acid (85 wt.%) and GC-grade heptane were supplied by Sigma–Aldrich, Malaysia. Methanol of highest purity (99.9%) and GC-grade hexane were obtained from Merck, Germany. All the received chemicals were used without any further purification or treatment. The characteristics of the as obtained CKO are presented in Table 2.

2.2. Reaction of CKO with methanol

Reactions of CKO with methanol using H_2SO_4 as a homogeneous catalyst were carried out under reflux by using a system of four round bottom flasks, each of 250 mL, mounted on heating mantles and connected to overhead condensers in series and equipped with digitally controlled magnetic stirrers. In a typical synthesis, a known amount of H_2SO_4 (0.5–3.5%), based on oil mass, was mixed with 16.64–35.55 mL of methanol and charged along with 88.842 g of CKO (total volume not exceeding 150 mL) into the reactor and stirred at 600 rpm. The composition of the products was analyzed by a gas chromatograph (GC; Shimadzu 2010 plus, Japan) equipped with a flame ionization detector (FID) and using a Nukol capillary column (15 m × 0.53 mm × 0.5 μm). Similarly, in order to compare the catalytic performance of H_2SO_4, an analogous experiment was conducted using H_3PO_4 as homogeneous catalyst adopting molar ratio of oil/methanol of 1:6 and allowed to proceed for 5 h at 65 °C. The reactions were carried out at temperatures ranging from 55 to 70 °C, monitored with a thermocouple sensor attached to a digital control interface for different reaction times. At the completion of the experiment, the reaction mixture was left to settle for 2 h before being transferred to a 15 mL centrifuge tube and methyl

ester was separated using a centrifuge at 2000g for 15 min. Once the two phases were separated, the excess alcohol in each phase was recovered and re-used.

2.3. Analysis of products

The conversion of CKO to biodiesel was valuated as a molar ratio of produced FAME per mole of feedstock. The evaluation was based on the determination of FAME content in the product as measured by GC analysis according to the EN14103 standard technique (Munari et al., 2007).

The analysis used methyl heptadecanoate as internal standard. The internal standard (IS) solution was prepared as 10.0 mg/mL of methyl heptadecanoate (C17:0) in heptane. The sample was prepared by adding 20 μL of reaction sample to 250 μL of IS solution. The injector and detector temperatures were fixed at 250 °C, whereas the oven temperature was set isothermally at 210 °C. Helium at 1.3 mL/min was used as carrier gas. A volume of 1 μL of the FAME sample containing IS solution was injected to the GC, and the FAME content was calculated according to (Munari et al., 2007).

3. Results and discussion

3.1. Effect of catalyst amount on CKO esterification

Fig. 1 shows the FAME content produced from CKO esterification when H_2SO_4 or H_3PO_4 was applied as liquid catalyst. When the catalyst amount was varied from 0.5% to 3.0%, a higher FAME yield was obtained with H_2SO_4 than H_3PO_4. The H_2SO_4-catalyzed process attained a maximum FAME content of 89.8% at a catalyst dosage of 2.0% sulfuric acid compared to a 15% yield when using 2% H_3PO_4. It was noted that addition of more than 2% sulfuric acid darkened the color of the product but amounts lower than 2% reduced the FAME yield.

3.2. Effect of alcohol to oil molar ratio

Alcohol/oil molar ratio was an important parameter controlling the conversion of triglycerides to methyl esters (Demirbas, 2009). Theoretically, the esterification reaction requires three moles of alcohol for each mole of oil; however, in practice, the molar ratio of the oil should be in excess of the stoichiometric ratio in order to drive the reaction towards ester formation. Fig. 2 presents the influence of different molar ratios (methanol/oil) on FAME yield using either H_2SO_4 or H_3PO_4. A ratio in the range of 4:1–8:1 was applied and, despite the low ratio of 6:1, the total methyl esters yield

Table 1
Properties of crude karanj oil (CKO) before esterification and test methods used.

Properties	Karanj oil	Test method
Density, g/mL 15 °C	0.924	EN ISO 3675
Kinematic Viscosity (40 °C), mm²/s	27.82	EN ISO 3104
Water content,%	10.20	EN ISO 12937
FFA,%	15.62	ASTM D5555
Saponification number, mg/g	186.4	ASTM D5558
Acid number, mg KOH/g oil	31.24	EN14104

The parameters depend on cultivation country and the season of the karanj tree used to produce CKO.

Table 2
Properties of karanj oil methyl esters and test methods used.

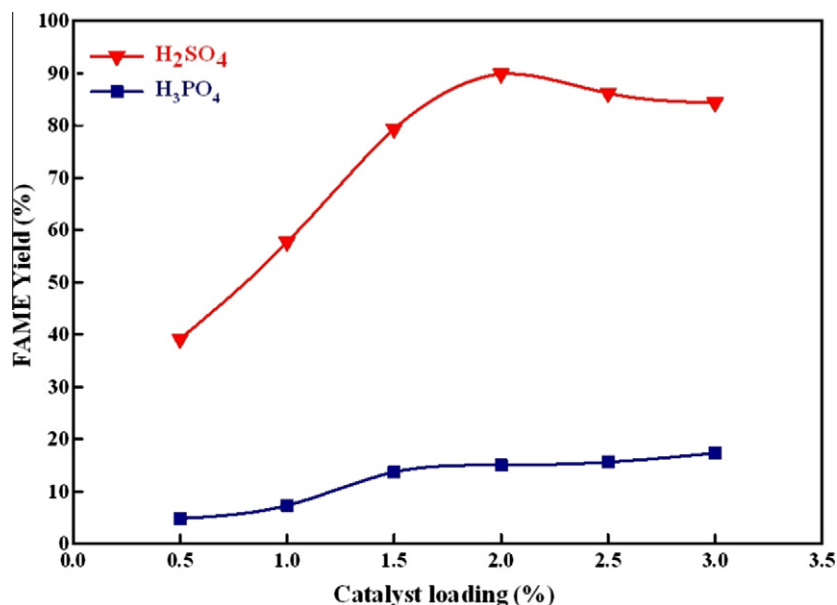| Property	CKO methyl ester	EN 14214/ASTM limits	Test methods
Acid value, KOH, mg g^{-1}	0.17	0.5 max	EN14104
Water content,%	0.038	0.05% max	EN ISO 12937
Kinematic viscosity (40 °C), mm²/s	4.66 ± 0.02	3.50–5.00	EN ISO 3104
Cloud point, °C	6	NS[a]	EN14214
Pour point, °C	3	NS[a]	ASTM D 97
Flash point, °C	212	120 min	EN22719
Density (15 °C), g cm^{-3}	0.883	0.860–0.900	EN ISO 3675
Group 1 metals (Na + K), mg/kg		0.5	EN14214
Refractive index (at 40 °C)	1.478	NS[a]	Atago refractometer model RX-5000a
Free glycerin, wt.%	0.0064	0.02	ASTM D6584
Total glycerin, wt.%	0.082	0.240	ASTM D6584
Phosphorus, mg/kg	0.04	<4–10	ASTM D4951
Monoglyceride content, wt.%	2.63	<0.8	EN14214
Diglyceride content, wt.%	0.78	<0.2	EN14214
Triglyceride content, wt.%	0.06	<0.2	EN14214

[a] NS: not specified.

Fig. 1. FAME content obtained with various amounts of H_2SO_4 catalyst. Reaction conditions: reaction temperature: 65 °C; molar ratio of oil/methanol: 1:6; reaction time: 5 h.
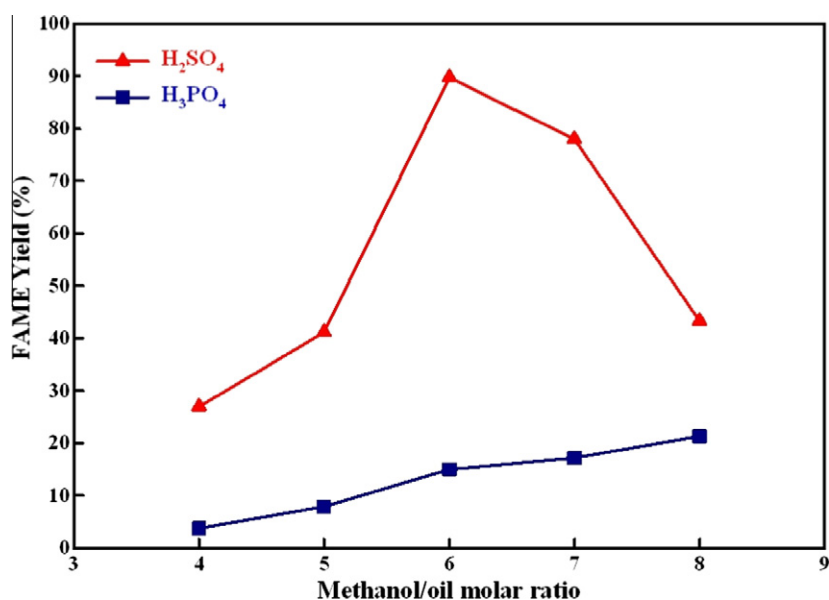

Fig. 2. Influence of molar ratio of methanol to feedstock on FAME content produced using H_2SO_4 as a catalyst. Reaction conditions: reaction temperature: 65 °C; reaction time: 5 h; catalyst loading: 2%.

exceeded 89.6% when sulfuric acid was used as catalyst as compared to about 18% attained using H_3PO_4. The increase in the molar ratio will not only drive the reaction forward, but also reduce the viscosity of the oil and improve in FAME quality. Increasing the alcohol/oil molar ratio beyond 6:1, resulted in a notable decrease in the yield of FAME as the reaction shifted towards hydrolysis. At a molar ratio of 3:1, soap formation was augmented and the reaction required more time to go to completion. The results obtained from this investigation were in good agreement with those reported by Karmee and Chadha (2005) for *P. pinnata* oil.

3.3. Effect of reaction temperature

The conversion of CKO to FAME increased as the temperature was raised (Fig. 3). A significant increase in FAME yield was observed when H_2SO_4 was used as compared to less than 24% FAME

yield obtained using H_3PO_4 under the same reaction conditions. The observed trend might be attributable to the differences in the acidic strength as well as the type of contributing acidic moieties of the two acids (De Pietre et al., 2010). Increase in temperature from 50 to 65 °C increased the FAME formation, while a further increasing to 70 °C resulted in only a minute increase in FAME yield. The methyl esters production profile obtained at different reaction temperatures was in agreement with those previously reported for the same feedstock (Mukta et al., 2009; Nabi et al., 2009).

3.4. Effect of reaction duration

Reaction time was the dominant parameter influencing the CKO conversion to methyl esters (Fig. 4). At a constant stirring rate, the FAME yield increased substantially with time for both acid catalysts. With H_2SO_4, there was a steady increase in the FAME yield to a
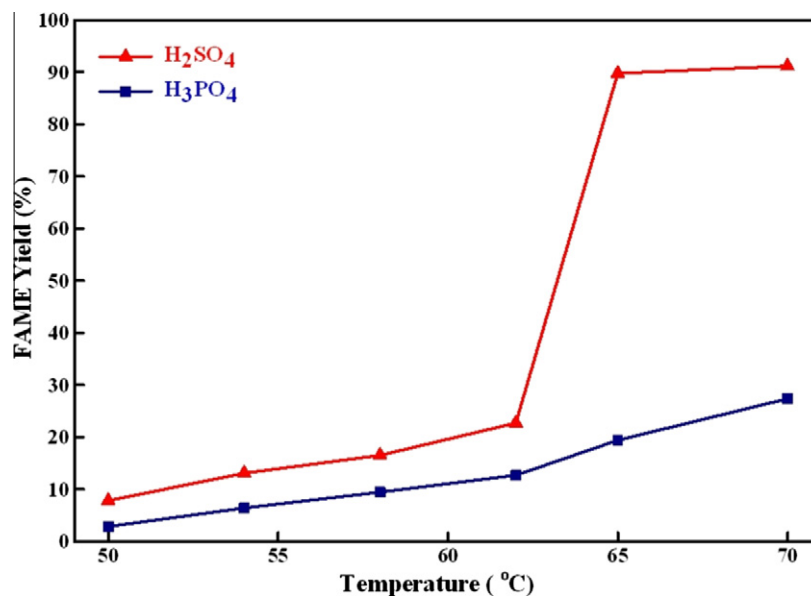
Fig. 3. Effect of temperature on FAME yield during the esterification of crude karanj oil (CKO) with methanol in the presence of H_2SO_4 or H_3PO_4 as catalysts. Reaction conditions: reaction time: 5 h; catalyst loading: 2%; molar ratio of oil/methanol: 1:6.
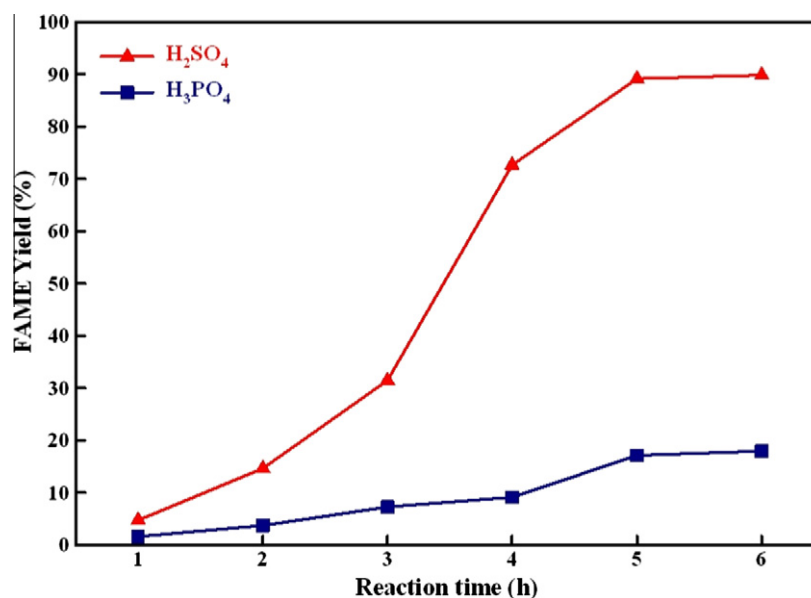

Fig. 4. Effect of reaction time on FAME yield during the esterification of crude karanj oil (CKO) with methanol in the presence of H_2SO_4 or H_3PO_4 as catalysts. Reaction conditions: reaction temperature: 65 °C; catalyst loading: 2%; molar ratio of oil/methanol: 1:6.

maximum of 89.6% after 5 h. In the same period, less than 20% FAME yield was observed when the reaction was catalyzed using H_3PO_4.

3.5. Properties of methyl esters obtained from CKO

Table 2 shows the results of the analysis and the test methods adopted for the determination of CKO methyl esters properties. The fuel properties of karanj methyl ester were similar to those of methyl esters obtained from other oils (Achtena et al., 2008), although there were exceptions such as its monoglyceride and diglyceride content.

3.6. Effect of CKO properties on the esterification reaction

Two of major properties that influence the production process of biodiesel are the FFA present in the oil and its water content.

As reported by Canakaci and Gerpen (2001), transesterification will not occur if FFA > 3%. The FFA content of CKO can be as high as 15.62% (equivalent to 31.24 mg of KOH/g sample) and water content as 10.2% depending on the source (Berchmans and Hirata, 2008; Karaj et al.,2008). The properties of the CKO used in the current study are given in Table 1. Product analysis revealed a reduction in the amount of FFA from 15.62 to 0.09%, the water content from 10.2 to 0.04% and the kinematic viscosity from 27.82 to 4.6 mm^2/s after 5 h. These values clearly highlight the high activity of the H_2SO_4 catalyst during the esterification of CKO.

4. Conclusions

Crude *P. pinnata* oil (CKO), is a promising feedstock for methyl esters synthesis and wide scale cultivation will contribute to support the biodiesel industry. The CKO methyl esters produced with

H_2SO_4 as catalyst meet the biodiesel qualities of the EN and ASTM standard and karanj oil could be therefore a cheap non-edible feedstock for biodiesel production.

Acknowledgements

References

Achtena, W.M.J., Verchot, L., Frankenc, Y.J., Mathijsd, E., Singhe, V.P., Aertsa, R., Muys, B., 2008. Jatropha bio-diesel production and use. Biomass Bioenerg. 32, 1063–1084.

Asakuma, Y., Maeda, K., Kuramochi, H., Fukui, K., 2009. Theoretical study of the transesterification of triglycerides to biodiesel fuel. Fuel 88 (5), 786–791.

Berchmans, H.J., Hirata, S., 2008. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. Bioresour. Technol. 99 (6), 1716–1721.

Canakaci, M., Gerpen, J.V., 2001. Biodiesel production from oils and fats with high free fatty acids. Am. Soc. Agr. Eng. 44, 1429–1436.

De Pietre, M., Almeida, L., Landers, R., Vinhas, R., Luna, F., 2010. H_3PO_4 and H_2O_4 treated niobic acid as heterogeneous catalyst for methyl ester production. Reac. Kinet. Mech. Cat. 99 (2), 269–280.

Demirbas, A., 2009. Progress and recent trends in biodiesel fuels. Energy Convers. Manage 50, 14–34.

Hameed, B.H., Goh, C.S., Chin, L.H., 2009. Process optimization for methyl ester production from waste cooking oil using activated carbon supported potassium fluoride. Fuel Process. Technol. 90 (12), 1532–1537.

Karaj, S., Huaitalla, Mendoza, R., Müller, Joachim, 2008. Physical, mechanical and chemical properties of *Jatropha curcas* L. seeds and kernels. Conference on International Agricultural Research for Development, Institute of Agricultural Engineering 440e, University of Hohenheim, Garbenstrasse 9, 70593 Stuttgart, Germany.

Karmee, S.K., Chadha, A., 2005. Preparation of biodiesel from crude oil of *Pongamia pinnata*. Bioresour. Technol. 96 (13), 1425–1429.

Kesari, V., Das, A., Rangan, L., 2010. Physico-chemical characterization and anti microbial activity from seed oil of *Pongamia pinnata*, a potential biofuel crop. Biomass Bioenerg. 34 (1), 108–115.

Lin, L., Cunshan, Z., Vittayapadung, S., Xiangqian, S., Mingdong, D., 2011. Opportunities and challenges for biodiesel fuel. Appl. Energ. 88 (4), 1020–1031.

Mukta, N., Murthy, I.Y.L.N., Sripal, P., 2009. Variability assessment in *Pongamia pinnata* (L.) Pierre germplasm for biodiesel traits. Ind. Crop. Prod. 29 (2-3), 536–540.

Mukta, N., Sreevalli, Y., 2010. Propagation techniques, evaluation and improvement of the biodiesel plant, *Pongamia pinnata* (L.) Pierre-A review. Ind. Crop. Prod. 31 (1), 1–12.

Munari, F., Cavagnino, D., Cadoppi, A., 2007. Thermo Fisher Scientific, Milan, Italy, Application Note: 10212.

Mustafa, B., 2011. Potential alternatives to edible oils for biodiesel production – A review of current work. Energ. Convers. Manage. 52 (2), 1479–1492.

Mustafa, C., 2007. Combustion characteristics of a turbocharged DI compression ignition engine fueled with petroleum diesel fuels and biodiesel. Bioresour. Technol. 98 (6), 1167–1175.

Nabi, M.N., Hoque, S.M.N., Akhter, M.S., 2009. Karanja (*Pongamia Pinnata*) biodiesel production in Bangladesh, characterization of karanja biodiesel and its effect on diesel emissions. Fuel Process. Technol. 90 (9), 1080–1086.

Naik, M., Meher, L.C., Naik, S.N., Das, L.M., 2008. Production of biodiesel from high free fatty acid Karanja (*Pongamia pinnata*) oil. Biomass Bioenerg. 32 (4), 354–357.

Ramos, M.J., Fernandez, C.M., Casas, A., Rodriguez, L., Perez, Ã., 2009. Influence of fatty acid composition of raw materials on biodiesel properties. Bioresour. Technol. 100 (1), 261–268.

Sharma, Y.C., Singh, B., 2008. Development of biodiesel from karanja, a tree found in rural India. Fuel 87 (8–9), 1740–1742.

Szulczyk, K.R., McCarl, B.A., 2010. Market penetration of biodiesel. Renew. Sust. Energ. Rev. 14 (8), 2426–2433.